



AFRL-AFOSR-VA-TR-2017-0090

Acquisition of Preparative Gel Permeation Chromatography for Research and Education in Energy Conversion and Nanocomposites

Zhiquan Lin
GEORGIA TECH RESEARCH CORPORATION
505 10TH ST NW
ATLANTA, GA 30318-5775

04/19/2017
Final Report

<p>DISTRIBUTION A: Distribution approved for public release.</p>

Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/RTB2

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Executive Services, Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.</p>					
1. REPORT DATE (DD-MM-YYYY) 19-04-2017		2. REPORT TYPE Final Performance		3. DATES COVERED (From - To) 15 Jan 2016 to 14 Jan 2017	
4. TITLE AND SUBTITLE Acquisition of Preparative Gel Permeation Chromatography for Research and Education in Energy Conversion and Nanocomposites				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER FA9550-16-1-0115	
				5c. PROGRAM ELEMENT NUMBER 61102F	
6. AUTHOR(S) Zhiquan Lin				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) GEORGIA TECH RESEARCH CORPORATION 505 10TH ST NW ATLANTA, GA 30318-5775 US				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AF Office of Scientific Research 875 N. Randolph St. Room 3112 Arlington, VA 22203				10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/AFOSR RTB2	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-AFOSR-VA-TR-2017-0090	
12. DISTRIBUTION/AVAILABILITY STATEMENT A DISTRIBUTION UNLIMITED: PB Public Release					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT The acquired Preparative Gel Permeation Chromatography (pGPC) and DMF GPC not only enhance the PI's ongoing DOD project on nanocomposites and energy pertinent to national defense, but also strategically stimulate and reinforce the research collaborations at the Georgia Institute of Technology between DOD- and NSF-funded projects in the areas of nanoscience listed in the proposal. The pGPC system possesses several advantages: the system allows extremely useful and monodisperse polymeric materials to be obtained from inexpensive, intractable, and sustainable sources; the system allows quantitative separation (gram quantities) and collection of several different sizes allowing for a systematic study of the properties of resulting synthesized nanostructures; and the system will greatly reduce the time necessary to develop novel, large quantities of many useful inorganic nanostructures (rod, tube, core/shell, hollow, etc.) by eliminating conventional, time consuming purification techniques. The acquired pGPC and DMF GPC systems are anticipated to enable new integration of research with education at all levels across a broad range of materials, and create important opportunities to expose and train undergraduates, women, and students from underrepresented communities as well as graduates and postdocs, on these characterization instruments.					
15. SUBJECT TERMS Equipment purchase, Gel Permeation Chromatography					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF	19a. NAME OF RESPONSIBLE PERSON LEE, CHARLES
a. REPORT	b. ABSTRACT	c. THIS PAGE			
Standard Form 298 (Rev. 8/98) Prescribed by ANSI Std. Z39.18					

DISTRIBUTION A: Distribution approved for public release.

Unclassified	Unclassified	Unclassified	UU	PAGES	19b. TELEPHONE NUMBER (Include area code) 703-696-7779
--------------	--------------	--------------	----	-------	---

Acquisition of Preparative Gel Permeation Chromatography for Research and Education in Energy Conversion and Nanocomposites

Zhiqun Lin

School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332

E-mail: zhiqun.lin@mse.gatech.edu

Final Report on the DURIP project: FA9550-16-1-0115 (01/15/2016-01/14/2017)

We acquired the following equipment over the past year with the DURIP support for research and education in nanocomposites, energy, and biotechnology.

Preparative Gel Permeation Chromatography from Shimadzu and Shodex

An essential tool in the systematic investigation of nanoscale materials employing complex polymer architectures is preparative gel permeation chromatography (Preparative GPC; pGPC). This technique can be used to separate polymers by their size in quantitative yields which can then be characterized, undergo further reaction into many inorganic nanostructures, or be incorporated directly into devices as is. This single instrument alone can have a truly transformative effect on the pace and applicability of nanoscale materials research and design because it can eliminate nanoscale size variability in complex macromolecular systems. This leads to reproducibility and reliability in material properties and therefore understanding; two important benchmarks for justifying the scale-up, commercialization and ultimate incorporation of novel technologies into our lives.

The acquired preparative gel Permeation chromatography (pGPC) from Shimadzu and Shodex features a high throughput design which allows gram quantity separation and collection of highly monodisperse polymer templates (cellulose, chitosan, lignin, and starch) from messy and often intractable raw sources with minimal waste of materials. It *not only* enhances the PI's ongoing DOD project on nanocomposites and energy pertinent to national defense, but also strategically stimulate and reinforce the research collaborations at the Georgia Institute of Technology between DOD- and NSF-funded projects in the areas of nanoscience and materials for energy.

The pGPC acquired from SHIMADZU SCIENTIFIC INSTRUMENTS is equipped with one LC-20AR HPLC Pump (MAX flow rate 20ml/min), one SIL-20A Prominence HPLC Autosampler (high-speed accurate injection of samples), one CBM-20A HPLC System Controller, one CTO-20A Prominence HPLC Column Ovens (large capacity, temperature up to 85°C), one RID-20A Refractive Index Detector, two Shodex HPLC Preparatory Scale Column (KF-2004), one LabSolutions Workstation Single-LC Software, and one LabSolutions Workstation GPC Software (**Figure 1**), and one FRC-10A



Figure 1. Preparative Gel permeation chromatography (pGPC) system from Shimadzu.

Fraction Collector (**Figure 2**). In addition, a Shodex HPLC Analytical Scale Column (KF-804, identical but downscale version of KF-2004) was ordered prior to ordering KF-2004 (preparatory scale) to ensure that the column type is adequate for fractionating cellulose-based polymers. THF is used as mobile phase and the columns are calibrated with polystyrene standards.

We have used the new pGPC to fractionate and characterize cellulose-based nonlinear polymers. The pGPC shows low PDI brominated cellulose that has been fractionated using this new system (**Figure 3**). Moreover, the brominated celluloses with different molecular weights are well resolved and separated, suggesting a good resolution of the acquired pGPC system. We plan to further narrow down the polydispersity (PDI) of brominated cellulose by controlling the elution time in future experiments.



Figure 2. FRC-10A Fraction Collector from Shimadzu Corporation, featuring a proprietary band function that enables obtaining accurate fractions even with varying peak elution times (Shimadzu Corporation)

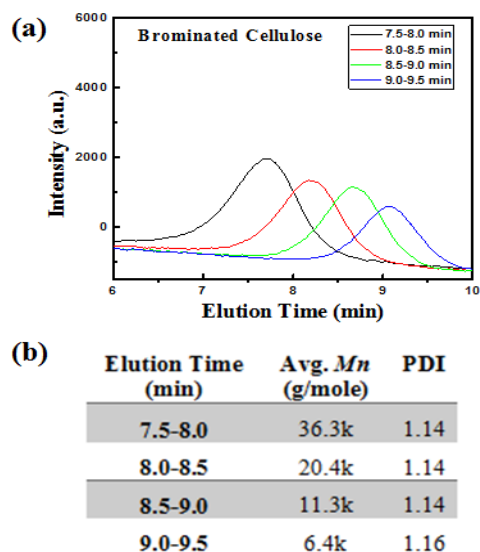


Figure 3. GPC of fractionated brominated cellulose using the newly acquired pGPC system.

DMF Gel Permeation Chromatography from Shimadzu and Phenomenex

Gel permeation chromatography (GPC) is a technique that is widely used for separating and analyzing polymers. It is one type of size exclusion chromatography (SEC) which separates analytes based on their different hydrodynamic volume or radius of gyration. This is different from other separation techniques which separate analytes on the basis of physical or chemical interaction. Separation is achieved via porous beads packed in the HPLC column. Analytes with smaller sizes can enter pores with smaller pore size, and therefore spend more time in more pores. The retention time of smaller analytes is longer in the column, which corresponds to lower molecular weight. By contrast, larger analytes eluted quickly from the column as they can only enter fewer pores due to their large size. All GPC columns have a range of molecular weight that can be measured. Molecular weight and molecular weight distribution (PDI) are two very important parameters for polymer, which can be readily obtained by the GPC measurement.

The GPC that uses dimethylformamide (DMF) as a solvent (hereafter referred to as DMF GPC) acquired from SHIMADZU SCIENTIFIC INSTRUMENTS is equipped with one LC-20AD HPLC Pump, one CTO-20A Column oven, one RID-20A, 120V, Refractive index detector, one CBM-20A Communications bus module, and the LabSolutions Single-LC software (**Figure 4**). The column oven can maintain stable temperature ($\pm 0.1^\circ\text{C}$) within column for consistent separation of molecules. RID-20A can effectively detect the change in reflective index

coming from concentration variation. Additionally, a Phenogel 5u 10E4A New Column 300 x 7.8 mm (in DMF) from *Phenomenex, Inc.* was purchased. The column is in DMF mobile phase and is designed to only measure molecules dissolvable in DMF with a molecular weight between 5K and 500K. The columns are calibrated with polystyrene standards. Due to the absorption of polymer and polar impurities onto the column which may affect the column performance after a certain period of usage (usually several years), an additional column of same type was also purchased for replacement when the original one fails.

We have been using DMF GPC to characterize nonlinear homopolymers and block copolymers with polar segments (**Figure 5**). The left panel shows a GPC trace of a star-like homopolymer, (i.e., star-like poly(4-vinyl pyridine; P4VP), possessing a molecular weight of 48, 000 g/mole and a narrow molecular weight distribution (PDI =1.12). The right panel display a GPC trace from star-like poly(4-vinyl pyridine)-block-poly(*tert*-butyl acrylate)-block-poly(ethylene oxide) (i.e., P4VP-*b*-PtBA-*b*-PEO), possessing a molecular weight of 59, 000 g/mole and a narrow molecular weight distribution (PDI =1.08). The peaks from two non-linear polymer samples are well resolved with narrow molecular weight distribution, signifying a good resolution of the acquired DMF GPC system.



Figure 4. Gel permeation chromatography (GPC) that runs DMF as mobile phase from Shimadzu.

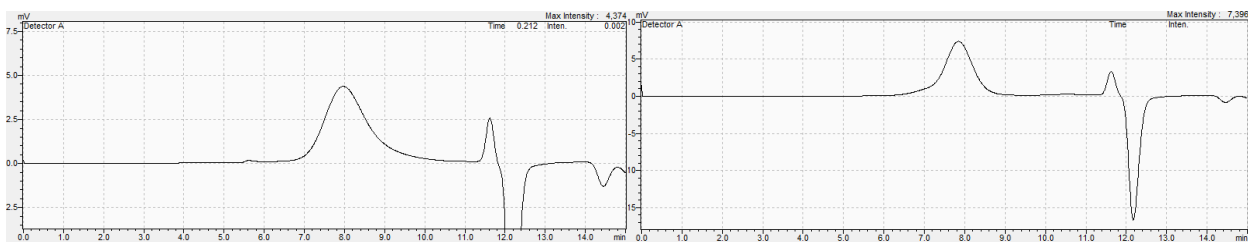


Figure 5. DMF GPC traces of star-like P4VP homopolymer (*left*), and star-like P4VP-*b*-PtBA-*b*-PEO triblock copolymer (*right*).

Dryfast 2042B Diaphragm Pumps from Gardner Denver Welch

High vacuum pumps are an essential technology required to prepare samples that are suitable for characterization by GPC as well as other techniques. In the case of our brominated cellulose, brominated beta-cyclodextrin and associated block copolymers, this is especially true. The synthesis processes of these materials necessitate high polarity and high boiling point solvents. These solvents need to be completely removed prior to material characterization because these residual solvents can damage chromatography columns and interfere with their analysis. In addition, residual solvents can affect the quality of subsequent nanocrystal templating.

The acquired pumps from Welch (a Gardner Denver company) are Dryfast© model 2042B-01 (**Figure 6**). These pumps have superior vacuum-drawing properties without the need to change out messy oil. Consequently they have long continuous run times for enabling

complete removal of solvent residues. The pumps are also fitted with a variable vacuum strength knob to precisely dial in on the necessary ultimate vacuum strength. High purity samples have been prepared using these pumps which has led to high quality nanocrystal synthesis results.

Research-Related Education

The acquired pGPC and DMF GPC will also serve as an educational wellspring for undergraduates, graduates and researchers who are most likely new and unfamiliar with this important technique. With an emphasis on characterization and practical knowledge education, Georgia Tech's materials science, chemical engineering, mechanical engineering and other curricula will benefit greatly from this resource.



Figure 6. Welch Dryfast 2042B high vacuum oil-free diaphragm pump.

Instrument Training for Students and Postdocs. One educational objective of this DURIP project is that the students using the instrument would gain a better understanding of the working principle of pGPC and DMF GPC and their capability of producing large scale pure polymeric fractions and molecular weights of polar polymers analytically, respectively. Students, postdocs and faculty alike will be able to receive training on the aforementioned pGPC and DMF GPC for use in their own research projects as well and serve as practical support for fundamentals taught in undergraduate classes in polymer science and engineering, characterization and separation across all engineering and scientific fields. Additional students and researchers from the School of Materials Science and Engineering, as well as from other schools throughout Georgia Tech, will also be using the acquired GPCs.

Teaching and outreach. Coincident with instrument training, the acquisition of the pGPC and DMF GPC will directly impact our planning efforts in the “*Nanostructured Materials*” course for a broad audience to enhance the class interactivity through incorporation of live demonstrations and video modules. Furthermore, as part of the School of Materials Science and Engineering’s ongoing efforts in educational outreach through the GHOST program (Georgia High School Outreach for Science and Technology), visiting high school students will also receive demonstrations on this equipment as part of interactive STEM-focused (Science, Technology, Engineering and Mathematics) tours and presentations to underscore the importance of scientists and engineers and convince them to consider careers in STEM fields. The goal of outreach activities is to increase the numbers of young people, especially minorities and women, who pursue advanced degrees in science and engineering.